PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

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PCT

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(PCT Rule 71.1)

Date of mailing *(day/month/year)*	12.01.2006
Applicant's or agent's file reference: 247	**IMPORTANT NOTIFICATION**

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/EP2004/009685	30.08.2004	29.09.2003

Applicant: UMICORE et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary report on patentability and its annexes, if any, established on the international application.

2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.

3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. **REMINDER**

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary report on patentability. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

The applicant's attention is drawn to Article 33(5), which provides that the criteria of novelty, inventive step and industrial applicability described in Article 33(2) to (4) merely serve the purposes of international preliminary examination and that "any Contracting State may apply additional or different criteria for the purposes of deciding whether, in that State, the claimed inventions is patentable or not" (see also Article 27(5)). Such additional criteria may relate, for example, to exemptions from patentability, requirements for enabling disclosure, clarity and support for the claims.

Name and mailing address of the international preliminary examining authority:	Authorized Officer
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Form PCT/IPEA/416 (January 2004)

247-WO-20060112-R

PATENT COOPERATION TREATY

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INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 247	**FOR FURTHER ACTION**	See Form PCT/IPEA/416
International application No. PCT/EP2004/009685	International filing date *(day/month/year)* 30.08.2004	Priority date *(day/month/year)* 29.09.2003
International Patent Classification (IPC) or national classification and IPC C22B19/04, C22B5/16, C22B9/22, C22B4/08, C22B13/02		
Applicant UMICORE et al.		

1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 6 sheets, including this cover sheet.
3. This report is also accompanied by ANNEXES, comprising:
   a. ☒ *sent to the applicant and to the International Bureau)* a total of 3 sheets, as follows:
      ☐ sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).
      ☐ sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.
   b. ☐ *(sent to the International Bureau only)* a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing and/or tables related thereto, in computer readable form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).

4. This report contains indications relating to the following items:

☒	Box No. I	Basis of the opinion
☐	Box No. II	Priority
☐	Box No. III	Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
☐	Box No. IV	Lack of unity of invention
☒	Box No. V	Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
☐	Box No. VI	Certain documents cited
☐	Box No. VII	Certain defects in the international application
☐	Box No. VIII	Certain observations on the international application

Date of submission of the demand	Date of completion of this report
12.04.2005	12.01.2006
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized Officer Bjoerk, P Telephone No. +49 89 2399-8452

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.
PCT/EP2004/009685

Box No. I Basis of the report

1. With regard to the **language**, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.

   ☐ This report is based on translations from the original language into the following language , which is the language of a translation furnished for the purposes of:
   - ☐ international search (under Rules 12.3 and 23.1(b))
   - ☐ publication of the international application (under Rule 12.4)
   - ☐ international preliminary examination (under Rules 55.2 and/or 55.3)

2. With regard to the **elements*** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report)*:

Description, Pages	
1-3, 5-8	as originally filed
4	filed with telefax on 17.08.2005
Claims, Numbers	
1-11	filed with telefax on 17.08.2005
Drawings, Sheets	
1/1	as originally filed

   ☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing

3. ☐ The amendments have resulted in the cancellation of:
   - ☐ the description, pages
   - ☐ the claims, Nos.
   - ☐ the drawings, sheets/figs
   - ☐ the sequence listing *(specify)*:
   - ☐ any table(s) related to sequence listing *(specify)*:

4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).
   - ☐ the description, pages
   - ☐ the claims, Nos.
   - ☐ the drawings, sheets/figs
   - ☐ the sequence listing *(specify)*:
   - ☐ any table(s) related to sequence listing *(specify)*:

* *If item 4 applies, some or all of these sheets may be marked "superseded."*

Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-11
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-11
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-11
	No:	Claims	

2. Citations and explanations (Rule 70.7):

see separate sheet

1. The application relates to a process for recovering metal values from a Zn-, Fe- and Pb-bearing residue whereby the residue is subjected to a flash or agitated bath fuming step, Zn- and Pb-bearing fumes are extracted to valorise Zn and Pb and either one or more of CaO, SiO_2 and MgO are added as a flux in order to obtain a final slag composition as defined through the three inequalities of claim 1. A single-chamber smelting and fuming reactor comprising a plasma fired tuyere attached to a plasma torch is also claimed in claim 10.

   Through the combination of forced agitation and the claimed slag composition, a rapid fuming process with improved yield and which can be run continuously can be achieved. It is said to be particularly suited for treating neutral leach residue or weak acid leach residue (p.3, l.17-25).

2. Claim 10 has been amended by specifying that the plasma tuyere is a "plasma fired tuyere attached to a plasma torch".

   The amendment finds a basis on page 5, line 29 ("equipped with submerged plasma fired tuyeres") and on page 6, lines 27-28 ("tuyere attached to a 1 MW air plasma torch") and is therefore allowable with regard to Art.19(2) PCT.

3. Reference is made to the following documents:

   D1: US-A-4 415 356
   D2: US-A-4 521 245
   D3: US-A-4 519 836
   D4: US-A-4 571 260
   D5: US-A-5 942 023

   D1 relates to an autogenous smelting process of sulfide material containing Cu, Ni, Co, Pb, Zn etc. (col.1, l.8-22). The autogenous smelting is preferably done by oxygen flash smelting (claim 2).

   D2 relates to flash smelting processing of sulphide Cu or Cu-Zn concentrates where

a highly basic molten slag with a maximum of 18 wt% SiO_2 is obtained (abstract).

D3 relates to flash smelting processing of Pb sulfide or Pb-Zn sulfide ores or concentrates where a molten slag with the following compositional requirements is obtained: $(SiO_2+Al_2O_3)/FeO$ = (0.67-1.22)/1 and (CaO+MgO)/FeO = (0.22-0.75)/1 (abstract).

D4 relates to a smelting process for recovering metal values from materials containing Sn and/or Zn whereby the slag is vigorously agitated by mechanical, pneumatic or electrical means, preferably by rotating the furnace (col.4, l.30-37). D4 also suggests a slag composition of 20-30% SiO_2, 25-35% CaO, <25% FeO and 5-10 $MgO+Al_2O_3$ (col.4, l.5-21).

D5 relates to a process for recovering metals from electric arc furnace (EAF) dust, using a reactor with a plasma tuyere as heat and gas sources, whereby the plasma is generated (18) below the slag level (30). Hazardous heavy metals are volatilized (32) (abstract and figure).

4. **Process claims 1-9**

Documents D1 to D4 show processes using a flash or agitated bath fuming step together with the extraction of Zn- and Pb-bearing fumes. However, none features slag compositions which fulfill the requirements set up in claim 1. Whereas D4 does discuss the fact that the skilled person would select a suitable slag from case to case (col.4, l.5-21), there is no hint in the available prior art to aim at a slag composition as presently claimed.

Consequently, the subject matter of claims 1 to 9 is seen to fulfill the requirements of Art.33(2) and (3) PCT.

5. **Apparatus claims 10-11**

Document D5 does not as such show a submerged tuyere attached to a plasma torch but merely the formation of a plasma arc zone 18 between the cathode formed by the

terminal end of the hollow graphite electrode 20 and the anode formed by the conductive plate 14. The "plasma gas" injected at 28 is inert gas which serves to cool the graphite electrode (col.3, l.19-39).

The arrangement of claim 10 is also not suggested in any of the remaining prior art.

Consequently, the subject matter of claims 10 and 11 is also seen to fulfill the requirements of Art.33(2) and (3) PCT.

Druckexemplar
Amended set of claims

Claims

1. Process for the valorisation of metal values in a Zn-, Fe- and Pb-bearing residue, comprising the steps of:

- subjecting the residue to a flash or agitated bath fuming step, thereby producing an Fe-bearing slag and Zn- and Pb-bearing fumes; and
- extracting the Zn- and Pb-bearing fumes and valorising Zn and Pb;

characterised in that either one or more of CaO, SiO_2 and MgO are added as a flux before or during the fuming step so as to obtain a final slag composition with:

$$\frac{[Fe]}{[SiO_2]}+\frac{[CaO]}{[SiO_2]}+\frac{[MgO]}{3}>3.5;$$

$$0.1<\frac{[CaO]}{[SiO_2]}<1.3;\text{ and}$$

$$6<[SiO_2]<22,$$

all concentrations being expressed in wt%.

2. Process according to claim 1, wherein the Zn-, Fe- and Pb-bearing residue is a neutral leach residue or a weak acid leach residue.

3. Process according to claim 2, characterised in that only one or both of dolomite and limestone are added as a flux.

4. Process according to any one of claims 1 to 3, characterised in that the concentration of MgO in the final slag is less than 5 wt%.

5. Process according to one of claims 1 to 4, characterised in that the Zn-, Fe- and Pb-bearing residue contains Cu and precious metals, and that, during the fuming step, a matte or alloy is produced containing a significant part of the Cu and a significant part of the precious metals.

6. Process according to any one of claims 1 to 5, characterised in that the Zn-, Fe- and Pb-bearing residue contains Ge, that a major part of the Ge is fumed together with Zn and Pb, and that it is subsequently separated.

7. Process according to claim 6, whereby the separation of Ge is performed by co-precipitation with Fe hydroxide or by addition of tannic acid.

8. Process according to any one of claims 1 to 7, whereby the process is performed in a reactor selected from the list consisting of a plasma flash furnace and a submerged lance furnace.

9. Process according to any one of claims 1 to 7, whereby the fuming step is performed in a reactor containing a molten phase, and comprising one or more plasma tuyeres as heat and gas sources, said tuyeres being arranged such that the plasma is generated under the surface of said molten phase.

10. Single-chamber smelting and fuming reactor for treating Zn-bearing residues, said reactor being designed to contain a molten slag phase up to a determined level, said reactor comprising a plasma fired tuyere attached to a plasma torch as heat and gas source, said tuyere being arranged such that the plasma is generated under said level.

11. Single-chamber smelting reactor according to claim 10, characterised in that the peripheral walls of the reactor are water-cooled.

Amended Page 4

with Fe hydroxide or by addition of tannic acid. Other useful separation techniques are solvent extraction and the use of ion-exchange resins.

The fuming process can be performed in reactors such as a plasma flash furnace and a submerged lance furnace. A single-chamber submerged plasma reactor comprising a plasma fired tuyere attached to a plasma torch as heat, gas and momentum source, the tuyere being arranged such that the plasma is generated under the surface of the molten slag phase, constitutes a novel concept in the art of Zn-fuming, and is particularly well suited for implementing the invented process, because of the high energy production coupled to a small quantity of generated gases. This reactor can be equipped with water-cooled peripheral walls, and can be operated in a continuous manner.

The details of the invention are now discussed.
The fuming step consists in the reduction-smelting of the residue, whereby reductants such as natural gas, LPG, coal or cokes, and possibly fluxes such as limestone ($CaCO_3$) dolomite ($MgCO_3$, $CaCO_3$) and silica (SiO_2) are added to produce a fast fuming slag with a high melting point. This high melting point corresponds to limited superheating of the slag. This greatly facilitates freeze-lining, i.e. the formation of a crust on the inner surface of the cooled vessel walls. Limited superheating results in the formation of a relatively stable and thick crust, ensuring good thermal insulation and efficiently protecting the vessel lining from corrosion. Heat losses towards the cooled walls are thus greatly reduced. Moreover, the relatively low silica content of the slag appears to enhance the fuming rate. A slag melting point of at least 1250 °C, and preferably of at least 1300 °C is recommended.

Figure 1 illustrates slag compositions on a ternary CaO-FeO-SiO_2 phase diagram. Representative prior art fayalite slags are shown as areas under references 1, 2 and 3. See "*Phase Equilibria and Thermodynamics of Zinc Fuming Slags*", E. Jak and P. Hayes, Canadian Metallurgical Quarterly, vol 41, No 2, pp 163 - 174, 2002. The slag composition according to this invention are shown as areas under reference 4 (for 0 wt% MgO) and references 4 + 5 (for 5 wt.% MgO).

In most cases, the Zn-bearing residue can be fluxed according to the above criteria using limestone and/or dolomite only. Minimising the